

DETERMINATION OF CHROMIUM OXIDATION STATES IN COAL COMBUSTION PRODUCTS BY XAFS SPECTROSCOPY

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ABSTRACT

Chromium XAFS spectroscopy has been used to determine the relative amounts of Cr(VI) and Cr(III) in ash samples obtained from coal combustion. The method, which is based on the relative heights of the pre-edge peaks for the different Cr oxidation states in XANES spectra, can be used to speciate as little as 50 ppm of chromium in ash. The results indicate that the fraction of Cr(VI) oxidation state present in combustion ash from commercial combustion plants is typically at or close to the detection limit (approx. 3% of the total chromium). Such findings provide justification for a reappraisal of whether or not chromium should be considered a significant HAP in coal combustion.

INTRODUCTION

Chromium is listed as one of eleven inorganic hazardous air pollutants (HAPs), the so-called "air-toxics", in Title III of the 1990 Amendments to the Clean Air Act (1), largely because of the well-known toxicological and carcinogenic properties of the hexavalent oxidation state of chromium (2). This oxidation state is virtually always found in nature and the environment in the form of chromate (CrO_4^{2-}) or dichromate ($\text{Cr}_2\text{O}_7^{2-}$) oxoanions. The other common oxidation state of chromium, Cr(III), is generally of much less concern to human health, and may in fact be essential in small quantities to mammals. Hence, in assessing potential health hazards posed by chromium in industrial emissions and wastes, it is clearly important that the chromium oxidation state be identified and determined quantitatively.

The different oxidation states of chromium in solids or any other state of matter can be readily distinguished in chromium X-ray absorption fine structure (XAFS) spectra by the intensity of the pre-edge peak (3,4,5). The pre-edge feature is generally very weak (typically less than 0.05 times the edge step) for trivalent chromium in an octahedral crystal-field of oxygen anions, whereas for hexavalent chromium oxoanions, the pre-edge peak is usually almost as intense as the edge-step. In this paper, a method for determining the oxidation states of chromium directly in solids is developed based on this difference in pre-edge peak intensity in chromium K-edge XAFS spectra and then the method is applied to the determination of chromium oxidation states in fly-ash and other products of coal combustion. Owing to the huge tonnages of coal used for electricity generation worldwide, coal combustion is viewed as a major potential source of release of many inorganic HAPs, including chromium, to the environment (6).

EXPERIMENTAL

Chromium K-edge XAFS spectroscopy:

XAFS spectroscopy is a synchrotron-based technique that provides information about the local structure and bonding around the absorbing element in a material from analysis of the fine structure associated with one of the element's characteristic X-ray absorption edges (7). For this study, experimental measurements were made at the chromium K-edge at both the National Synchrotron Light Source at Brookhaven National Laboratory, New York, and at the Stanford Synchrotron Radiation Laboratory, Stanford University, CA. Similar experimental practices were used at both synchrotrons. To record the chromium K-edge XAFS spectra, the monochromator was stepped from about 100 eV below the edge to as much as 1,000 eV above the edge and the intensity of the monochromatic x-ray beam before and after absorption by the sample was measured as a function of energy. All spectra were calibrated with respect to the first inflection point in the absorption spectrum of a thin chromium metal foil. This calibration point, which occurs at 5,989 eV, defines the zero-point of energy in the XAFS spectra shown in Figure 1 and other figures in this paper. The absorption spectra were measured in three different ways depending on the concentration of chromium in the material under investigation. For concentrated samples ($\text{Cr} > 10\text{wt}\%$), measurements were made in absorption geometry, in which the intensity of the X-ray beam after attenuation by the absorption process in the sample was compared to the incident X-ray intensity. These measurements were made with ion chambers. For more dilute samples with chromium contents less than 5 wt% but more than about 0.1 wt% (1000 ppm), the intensity of the fluorescent X-rays emitted by the sample in response to the absorption process was measured with a Lytle detector (8). Finally, for chromium in ash samples, in which the concentration of chromium is very dilute (typically between 50 and 500

ppm), measurements were made using a 13-element germanium detector that collected X-rays only in a electronically gated energy interval set for fluorescent chromium X-rays (9). For the fluorescent measurements, a vanadium filter was normally used in association with Soller slits to enhance the signal/noise ratio. Spectral scans of about 30 mins were sufficient for most samples, except those for which the chromium content was much less than 500 ppm. Depending on the actual chromium concentration of such dilute samples, up to 10 separate scans were accumulated and summed to give a single spectrum.

The spectra have been analyzed in a conventional manner that is well described in the literature (7). Basically, the spectra are split into two distinct regions: a near-edge region that includes the fine structure associated with the edge itself, and an extended fine-structure region that consists of the weak oscillatory structure that may persist to as much as 1,000 eV above the edge. These two regions give rise to the X-ray absorption near-edge structure (XANES) spectra and the extended X-ray absorption fine structure (EXAFS) spectra, respectively. The XANES spectrum is generally used as a "fingerprint" to identify the form or forms of the element in the material under investigation, whereas the EXAFS region can be mathematically manipulated to yield a "radial structure function" (RSF) from which the local structure around the absorbing element may be inferred. In this work, only the XANES spectra will be discussed further as the EXAFS region of the spectrum is not used to determine the chromium oxidation states.

Determinative Method:

A calibration method for the XANES pre-edge peak was developed by measuring the XANES spectra of carefully prepared mixtures of potassium chromate (K_2CrO_4) and potassium chromium(III) alum sulfate ($KCr(SO_4)_2 \cdot 12H_2O$). Except for different standards in the mixtures, the current method is similar that described by Bajt et al. (4). The mixtures were prepared so that Cr(VI) constituted 0%, 5%, 10%, 15%, 20%, 25%, 50%, 75%, and 100% of the total chromium in the samples. In addition, the total chromium contents of all mixtures were reduced to 4.0 wt% by dilution of the mixtures in boric acid (HBO_3).

Edge-step normalized XANES spectra of chromium in the boric acid pellets are shown in Figure 1 for all nine calibration mixtures. The spectra are offset vertically to highlight the systematic changes that occur with increasing Cr(VI) content. The pre-edge feature between 0 and 10 eV is the spectral feature that shows the most change and it is also the easiest to quantify. As shown by most Cr(III) standards, the pre-edge feature of the end-member K-Cr alum sulfate consists of two peaks: a weak peak at about 1.5 - 2.0 eV and a second, even weaker peak at about 4.0 eV. The chromate pre-edge peak consists of a single intense peak at about 4.0 eV. To quantify these changes, a least-squares iterative fitting program was used that fits the peaks to a mixed lorentzian-gaussian line shape and the background to an arctangent function. This program returns information on the intensity, width, and position of the peaks once the least-squares fitting has converged. These data are summarized in Table 1 for the pre-edge regions shown in Figure 1 and calibration curves were then prepared from the data for the peak at 4.0 eV. The variation of the normalized height of the pre-edge feature with Cr(VI) content was linear with a correlation coefficient (r^2) in excess of 99% (Figure 2).

TABLE 1
Results from Least-Squares Fitting of Calibration Data

Cr(VI)/Total Cr	Peak at 2.0 eV			Peak at 4.0 eV		
	Height	Width	Area	Height	Width	Area
0	0.035	1.855	0.064	0.013	1.855	0.024
5	0.033	1.974	0.065	0.042	1.983	0.083
10	0.032	2.306	0.073	0.086	2.058	0.176
15	0.037	2.527	0.093	0.116	1.968	0.228
20	0.034	2.000	0.068	0.170	2.070	0.351
25	0.036	2.167	0.078	0.199	2.087	0.415
50	0.024	2.000	0.048	0.404	2.200	0.880
75	---	---	---	0.620	2.200	1.364
100	---	---	---	0.823	2.280	1.876

It should be understood that although the derived calibration curve has an extremely small standard error associated with it (<1% Cr), there are other significant sources of uncertainty that need to be addressed. These include possible variation of the pre-edge intensity with site distortion (10), thick absorber effects (7), dead-time corrections in the 13-Ge element detector

(9), and appropriateness of K_2CrO_4 as the standard for Cr(VI) in ash. Such factors were not explicitly considered in the method described by Bajt et al. (4).

To circumvent all of these sources of uncertainty, it was decided to use the Cr(III) pre-edge peak at lower energy (1.5 eV) to calibrate any possible peak intensity enhancement due to these effects. This pre-edge peak is approximately three times the intensity of the pre-edge peak at about 3.5 - 4.5 eV for most Cr^{3+} materials. This relationship can then be used to define a zero Cr(VI) baseline that allows for possible experimental saturation effects and site distortion phenomena and, hence, for more precise estimation of the Cr(VI) content.

By using this approach for defining the intercept from the normalized height, h_2 , of the peak at about 1.5 - 2.5 eV, a generalized equation can be derived for the relationship between the normalized height, h_4 , of the peak at about 3.5 - 4.5 eV and the concentration of Cr(VI) in a sample, as follows:

$$\%Cr(VI) = 110 (h_4 - h_2/3) \quad (1)$$

The slope is derived not only from the linearity of the calibration data presented in Table 1, but is an average value that also takes into account the variation in pre-edge peak height exhibited by different chromate compounds. Consequently, any value of Cr(VI) determined from this equation has an uncertainty of up to $\pm 10\%$, because the probable forms of Cr(VI) in combustion ash samples are likely not well represented by any one chromate compound.

RESULTS AND DISCUSSION:

We have applied the above equation to measurements made on the Cr XANES spectra to estimate approximate values for Cr(VI) in various ash samples derived from coal combustion. Figure 3 shows the chromium XANES spectra for three commercial and one laboratory ash samples. Parameters (normalized height, width, area, position) for the pre-edge peaks were quantified by least-squares fitting using the program EDGFit. Examples of the least-squares fitting are shown in Figure 4. The percentage of Cr(VI) present in the sample was estimated from the pre-edge peak heights using the above relationship (equation 1). The results of such fitting are summarized in Table 2 for all ash and slag samples examined.

Based on the spectra shown in Figures 3 and 4 and the results listed in Table 2 derived from least-squares fitting of the pre-edge peak, none of the fly-ash or bottom ash samples from either commercial coal combustion plants or laboratory experiments appears to contain significant Cr(VI) present in the samples, with the possible exception of the Pittsburgh drop-tube sample. All the results showed that the determined Cr(VI) content was typically around 1 - 5% of the total chromium. However, there is an estimated experimental uncertainty of $\pm 3 - 5\%$ in such determinations from uncertainty in the determined heights of the peaks in the fitting procedure. Hence, 0% Cr(VI) is almost as significant a result as the determined value in many instances.

TABLE 2
Results from Least-Squares Fitting of Cr XANES of Combustion Ashes

Ash Sample	Peak at 2.0 eV		Peak at 4.0 eV		Estimated Content of %Cr(VI)
	Height	Pos'n	Height	Pos'n	
<u>Commercial:</u>					
Cooper FA	0.044	1.5	0.030	3.8	2
NIST SRM 1633b	0.044	1.4	0.038	3.8	3
LET FA-1	0.050	2.4	0.034	4.1	2
LET BA-1	0.054	1.5	0.055	3.9	4
LET BA-2	0.040	1.6	0.035	3.3	3
LGE FA	0.042	1.9	0.054	3.9	5
LGE BA	0.053	2.1	0.033	4.1	1
<u>Laboratory:</u>					
Univ. Arizona Combuster:					
51-14-Coarse	0.063	2.3	0.061	4.8	3
51-14-Med	0.045	2.0	0.041	4.4	3
51-14-Fine	0.040	1.8	0.046	4.2	4
47-07-Coarse	0.039	1.9	0.020	4.4	1
PSIT Drop Tube:					
Pittsburgh Ash	0.031	1.7	0.091	3.6	9
Illinois #6 Ash	0.036	1.9	0.047	3.7	4

The Pittsburgh drop-tube sample (DECS-12) exhibits a value for Cr(VI), $9 \pm 3\%$, that is significantly higher than those determined for other ash samples. It should be noted that the Cr XANES spectrum (Fig. 3) for this sample was also one of the best quality so that this higher value can not be due to larger than normal experimental uncertainty. It is likely that this result can be attributed to the fact that the drop-tube experiments are normally carried out in excess air in comparison to conditions in the larger-scale combustors. Hence, a slight enhancement in the Cr(VI)/Cr(III) ratio may not be unusual given such circumstances. However, this observation would also appear to imply that conditions of coal combustion are not far removed from those that could result in significant formation of Cr(VI): Unusual furnace conditions (e.g. low temperatures, high oxygen fugacity) or possibly unusual slag chemistry may yet be found that result in the formation of significant Cr(VI) in combustion ash materials.

CONCLUSIONS

A direct and nondestructive method has been developed for speciating chromium in solid samples based on the normalized peak-height of the pre-edge feature in chromium XANES spectra. The method is capable of determining the relative percentages of the two major chromium oxidation states, with an uncertainty of $\pm 10\%$, down to as little as 5-10 ppm of chromium in relatively X-ray transparent solids such as combustion ash or coal. The only preparation necessary is to ensure that the sample has a particle size less than about 200 mesh (0.075 mm top size) and that it is representative over an X-ray beam spot size of between 4 and 10 mm². No chemical separation is done on the sample nor is any method of pre-concentration used prior to analysis.

This spectroscopic method shows that the Cr(VI) content of all commercial ash samples so far examined is at or below the detection limit for Cr(VI), estimated to be about 3 - 5% of the total chromium, depending on concentration. These results are in agreement with data for fly-ash samples determined by ICP-AES, in which the Cr(VI) is complexed and extracted by ammonium hydroxide (11). Such findings imply that the behavior of chromium in coal combustion should be re-examined carefully to assess whether or not this element is a significant HAP. However, as the current results indicate for ash samples from small-scale laboratory combustion experiments, typical combustion conditions appear to be quite close to those that could promote formation of significant Cr(VI).

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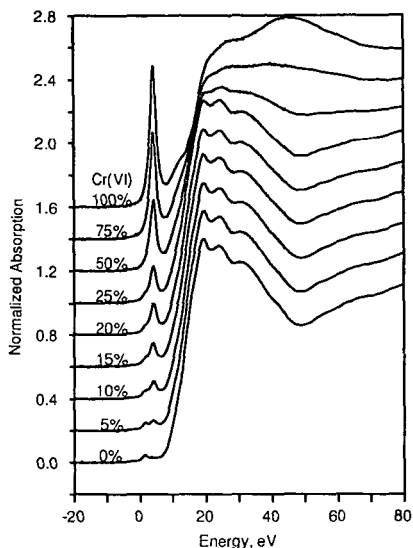


Figure 1: Chromium XANES spectra for mixtures of K-Cr(III) alum sulfate and $K_2Cr(VI)O_4$.

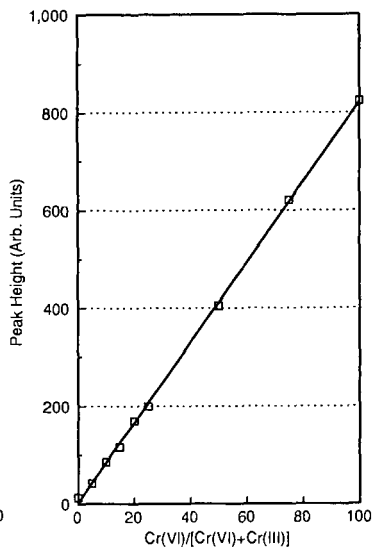


Figure 2: Calibration curve based on normalized peak height of least-squares fitted pre-edge peaks in Figure 1.

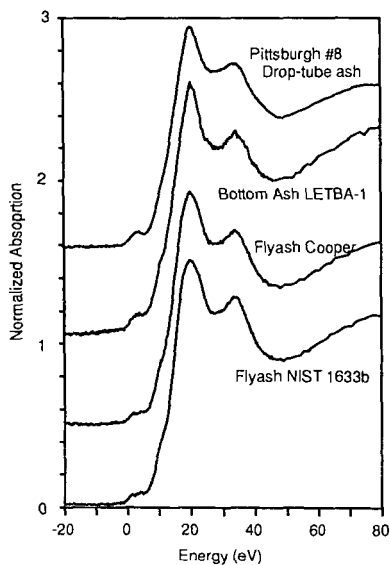


Figure 3: Chromium K-edge XANES spectra for three commercial ash products and a laboratory drop-tube ash.

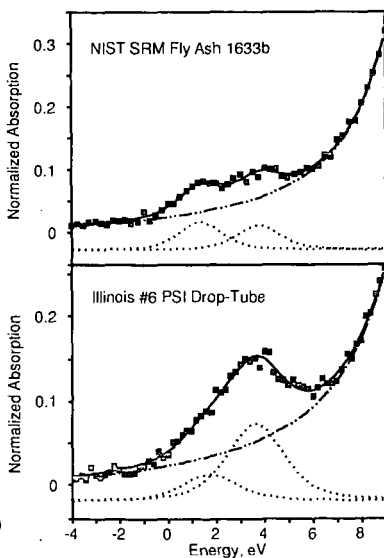


Figure 4: Examples of least-squares fitting of the pre-edge peak present in Cr XANES spectra of ash samples.